

On the gradient for metallic systems with a local basis set

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Abstract

The analytical gradient for periodic systems is presented, for the case of metallic systems. The total energy and the free energy are computed on the Hartree-Fock or density functional level, with the wave function being expanded in terms of Gaussian type orbitals. The expression for the gradient is similar to the case of insulating systems, when no thermal broadening is applied. When the occupation of the states is according to the Fermi function, then the gradient is consistent with the gradient of the free energy. By comparing with numerical derivatives, examples demonstrate that a reasonable accuracy is achieved.

Keywords: analytical gradient, metals, free energy

1. Introduction

Today, analytical gradients are widely available in electronic structure codes. In the case of molecules, gradients with respect to the nuclear position are required, and in solids, in addition, gradients with respect to the cell parameters. Periodic systems often employ plane waves as basis functions, but local basis sets are also popular [1, 2]. Local basis sets, usually atom centered, require the calculation of derivatives of the basis functions with respect to the nuclear positions, the Pulay forces [3, 4, 5]. This holds for the case of molecular and periodic [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21] systems. Periodic systems have the feature that metallic ground states are a possible solution. Metallic systems are more difficult to treat than insulators, because the position of the Fermi energy has to be determined, and

the integration is only over a part of the Brillouin zone and thus more difficult than in the case of insulators. In the case of Hartree-Fock theory, there are further problems due to the vanishing density of states at the Fermi level [22] and the slow decay of the density matrix at zero temperature (this is however less problematic at finite temperature where the decay is exponential [23]). This has motivated the use of a screened Coulomb operator for the exchange interaction [24]. For an overview of calculations for metals with Gaussian basis sets, see [25]. Some time ago, it had been argued that the gradient requires an extra term due to the shape of the Fermi surface [26]. This will be discussed in the present work, and it appears that this term is spurious. Numerical tests indicate that a reasonable accuracy can be achieved, and the analytical derivatives agree well with numerical derivatives of the free energy.

2. Formalism

2.1. Zero temperature

The analytical gradients for periodic systems, on the Hartree-Fock level, were introduced by [6, 7]. A little later, an article suggested that an extra term should appear in the case of metals [26], which will be reconsidered in the following. A notation similar to [6, 7, 26] is used, for the sake of simplicity. This corresponds to the case of one dimensional periodicity, but the argument can analogously be transferred to two and three dimensions. The notation is similar to the molecular case [27], apart from the summation over the lattice vectors.

The crystalline orbitals $\Psi_n(\vec{r}, k)$, with the band index n and the k -point k are expanded in linear combinations of Bloch functions:

$$\Psi_n(\vec{r}, k) = \sum_{\mu} c_{\mu n}(k) \psi_{\mu}(\vec{r}, k) \quad (1)$$

with

$$\psi_{\mu}(\vec{r}, k) = \frac{1}{\sqrt{N}} \sum_j \exp(ikja) \chi_{\mu}^j(\vec{r}) \quad (2)$$

where N is the number of unit cells in the macro-lattice, or equivalently the number of reducible k -points, and $\chi_{\mu}^j(\vec{r})$ being a basis function (e.g. a Gaussian) in cell j . The overlap matrix element between orbital μ in cell 0 and ν in cell j is obtained as

$$S_{\mu\nu}^{0j} = \int \chi_{\mu}^{0*}(\vec{r}) \chi_{\nu}^j(\vec{r}) d^3r \quad (3)$$

and its Fourier transform as

$$S_{\mu\nu}(k) = \sum_j \exp(ikja) S_{\mu\nu}^{0j} \text{ and } S_{\mu\nu}^{0j} = \frac{1}{N} \sum_k S_{\mu\nu}(k) \exp(-ikja) \quad (4)$$

with the cell parameter a . Because of the orthonormality of the crystalline orbitals, it holds:

$$\sum_{\mu\nu} c_{\mu m}^*(k) S_{\mu\nu}(k) c_{\nu n}(k) = \delta_{mn} \quad (5)$$

The total energy per primitive unit cell is expressed as in [6, 7, 26] as

$$E = \frac{1}{2} \sum_{j,\mu,\nu} (H_{\mu\nu}^{0j} + F_{\mu\nu}^{0j}) P_{\nu\mu}^{j0} + E(NR) \quad (6)$$

with $H_{\mu\nu}^{0j}$ being the one-electron part of the Fock matrix element, $F_{\mu\nu}^{0j}$ the corresponding Fock matrix element:

$$F_{\mu\nu}^{0j} = H_{\mu\nu}^{0j} + \sum_{h,l,\tau,\lambda} P_{\lambda\tau}^{lh} \langle \mu\nu |^{0j} |_{\tau\lambda}^{hl} \rangle \quad (7)$$

with $\langle \mu\nu |^{0j} |_{\tau\lambda}^{hl} \rangle = \langle \tau\lambda |^{hl} |_{\mu\nu}^{0j} \rangle$ being the two-electron integral:

$$\begin{aligned} \langle \mu\nu |^{0j} |_{\tau\lambda}^{hl} \rangle &= \int \chi_{\mu}^{0*}(\vec{r}_1) \chi_{\nu}^j(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \chi_{\tau}^{h*}(\vec{r}_2) \chi_{\lambda}^l(\vec{r}_2) d^3r_1 d^3r_2 \\ &- \frac{1}{2} \int \chi_{\mu}^{0*}(\vec{r}_1) \chi_{\lambda}^l(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \chi_{\tau}^{h*}(\vec{r}_2) \chi_{\nu}^j(\vec{r}_2) d^3r_1 d^3r_2 \end{aligned} \quad (8)$$

$P_{\nu\mu}^{j0}$ is the corresponding density matrix element, and the nuclear repulsion energy is labelled as $E(NR)$. Strictly speaking, some of the terms such as $E(NR)$ are divergent for a periodic system, and a formulation based on e.g. the Ewald and related methods would be more suitable [28, 29]. However, the main issue of the present paper can easiest be demonstrated with a notation

consistent with references [6, 7, 26], and convergence issues of the Coulomb sums shall be ignored. The Hartree-Fock equations for periodic systems [30, 31] are:

$$\sum_{\nu} F_{\mu\nu}(k) c_{\nu n}(k) = \sum_{\nu} S_{\mu\nu}(k) c_{\nu n}(k) \epsilon_n(k) \quad (9)$$

with $\epsilon_n(k)$ being the eigenvalues.

For metallic systems, the density matrix is expressed as in [26]:

$$\begin{aligned} P_{\nu\mu}^{j0} &= \frac{2}{N} \sum_{k,n} \exp(ikja) c_{\mu n}^*(k) c_{\nu n}(k) \theta(E_F - \epsilon_n(k)) \\ &= \frac{1}{N} \sum_k P_{\nu\mu}(k) \exp(ikja) \end{aligned} \quad (10)$$

with the Fermi energy E_F and the Heaviside function θ . The factor 2 is due to the summation over the 2 spin states. Due to translational invariance, relations such as $P_{\nu\mu}^{hl} = P_{\nu\mu}^{h-l\ 0}$ hold. The derivative of the total energy with respect to a geometrical parameter $\frac{\partial E}{\partial X}$ is then obtained as in [6, 7]:

$$\begin{aligned} \frac{\partial E}{\partial X} &= \sum_{j,\mu,\nu} \frac{\partial H_{\mu\nu}^{0j}}{\partial X} P_{\nu\mu}^{j0} + \frac{1}{2} \sum_{j,\mu,\nu} \sum_{h,l,\tau,\lambda} P_{\lambda\tau}^{lh} P_{\nu\mu}^{j0} \frac{\partial ({}^{0j}_{\mu\nu} || {}^{hl}_{\tau\lambda})}{\partial X} \\ &- \sum_{j,\mu,\nu} \frac{\partial S_{\mu\nu}^{0j}}{\partial X} \sum_{k,n} \frac{2}{N} \exp(ikja) c_{\mu n}^*(k) c_{\nu n}(k) \theta(E_F - \epsilon_n(k)) \epsilon_n(k) + \frac{\partial E(NR)}{\partial X} \end{aligned} \quad (11)$$

The expression

$$\sum_{k,n} \frac{2}{N} \exp(ikja) c_{\mu n}^*(k) c_{\nu n}(k) \theta(E_F - \epsilon_n(k)) \epsilon_n(k) \quad (12)$$

corresponds to the energy weighted density matrix.

In the following, the derivative of the θ function shall be considered in more detail. When computing the gradient with respect to a geometrical parameter X , then the derivative term G due to the Heaviside function is obtained as

$$\begin{aligned}
G &= \sum_{m,\alpha,\beta} \frac{\partial E}{\partial P_{\beta\alpha}^{m0}} \frac{\partial P_{\beta\alpha}^{m0}}{\partial \theta(E_F - \epsilon_n(k))} \frac{\partial \theta(E_F - \epsilon_n(k))}{\partial X} \quad (13) \\
&= \sum_{m,\alpha,\beta} \frac{1}{2} \left((H_{\alpha\beta}^{0m} + F_{\alpha\beta}^{0m}) + \sum_{h,l,\tau,\lambda} P_{\lambda\tau}^{hl} ({}^{0m}_{\alpha\beta} || {}^{lh}_{\tau\lambda}) \right) \frac{\partial P_{\beta\alpha}^{m0}}{\partial \theta(E_F - \epsilon_n(k))} \frac{\partial \theta(E_F - \epsilon_n(k))}{\partial X} \\
&= \sum_{m,\alpha,\beta} F_{\alpha\beta}^{0m} \frac{\partial P_{\beta\alpha}^{m0}}{\partial \theta(E_F - \epsilon_n(k))} \frac{\partial \theta(E_F - \epsilon_n(k))}{\partial X} \\
&= \sum_{m,\alpha,\beta} \frac{2}{N} F_{\alpha\beta}^{0m} \sum_k \sum_n \exp(ikma) c_{\alpha n}^*(k) c_{\beta n}(k) \delta(E_F - \epsilon_n(k)) \left[\frac{\partial E_F}{\partial X} - \frac{\partial \epsilon_n(k)}{\partial X} \right] \\
&= \frac{2}{N} \sum_{k,n} \sum_{\alpha,\beta} F_{\alpha\beta}(k) c_{\alpha n}^*(k) c_{\beta n}(k) \delta(E_F - \epsilon_n(k)) \left[\frac{\partial E_F}{\partial X} - \frac{\partial \epsilon_n(k)}{\partial X} \right] \\
&= \frac{2}{N} \sum_{k,n} \sum_{\alpha,\beta} c_{\alpha n}^*(k) S_{\alpha\beta}(k) c_{\beta n}(k) \epsilon_n(k) \delta(E_F - \epsilon_n(k)) \left[\frac{\partial E_F}{\partial X} - \frac{\partial \epsilon_n(k)}{\partial X} \right] \\
&= \frac{2}{N} \sum_{k,n} \epsilon_n(k) \delta(E_F - \epsilon_n(k)) \left[\frac{\partial E_F}{\partial X} - \frac{\partial \epsilon_n(k)}{\partial X} \right] \\
&= \frac{2}{N} \sum_{k,n} E_F \delta(E_F - \epsilon_n(k)) \left[\frac{\partial E_F}{\partial X} - \frac{\partial \epsilon_n(k)}{\partial X} \right] = \frac{2}{N} \sum_{k,n} E_F \frac{\partial \theta(E_F - \epsilon_n(k))}{\partial X}
\end{aligned}$$

Note that in reference [26], $(H_{\alpha\beta}^{0j} + F_{\alpha\beta}^{0j})$ appears instead of $2F_{\alpha\beta}^{0j}$, and this appears to be incorrect (see also the related calculation in [27]). With the number of electrons in the unit cell n_0 , it follows as in [26]:

$$\begin{aligned}
n_0 &= \sum_{\mu,\nu,j} S_{\mu\nu}^{0j} P_{\nu\mu}^{j0} \quad (14) \\
&= \sum_{\mu,\nu,j} S_{\mu\nu}^{0j} \frac{2}{N} \sum_{k,n} \exp(ikja) c_{\mu n}^*(k) c_{\nu n}(k) \theta(E_F - \epsilon_n(k)) \\
&= \frac{2}{N} \sum_{\mu,\nu} \sum_{k,n} S_{\mu\nu}(k) c_{\mu n}^*(k) c_{\nu n}(k) \theta(E_F - \epsilon_n(k)) = \frac{2}{N} \sum_{k,n} \theta(E_F - \epsilon_n(k))
\end{aligned}$$

and, as the particle number is fixed, $\frac{\partial n_0}{\partial X} = 0$, and therefore from equation 13, $G = 0$ is obtained: there is thus no extra term due to the step function,

and the same expression as for the case of insulators [6, 7] can be used for the derivatives with respect to geometrical parameters.

2.2. Finite temperature

An additional problem in the case of metals is the numerical integration of integrals over the occupied part of the Brillouin zone. This problem requires k -point meshes as large as possible. A more efficient way is to apply a finite temperature scheme. The calculation can then be theoretically based on finite temperature density functional theory [32]. The occupation numbers can be chosen e.g. according to the Fermi function. Gaussian broadening is another popular scheme [33, 34, 35]. Further schemes (Lorentzian broadening, a step function) had been discussed in [36]. The Fermi function has the advantage that the computed free energy has a direct physical meaning, as it contains the electronic contribution to the free energy; contributions due to e.g. phonons are however missing (see, e.g. [37]). The Fermi function is defined as

$$f_{k,n} = \frac{1}{1 + \exp((\epsilon_n(k) - E_F)/k_B T)} \quad (15)$$

with the Boltzmann constant k_B . A small finite temperature can be introduced, so that the density matrix becomes

$$P_{\mu\nu}^{0j} = \frac{2}{N} \sum_{k,n} \exp(-ikja) c_{\nu n}^*(k) c_{\mu n}(k) f_{k,n} \quad (16)$$

and

$$P_{\mu\nu}(k) = 2 \sum_n c_{\nu n}^*(k) c_{\mu n}(k) f_{k,n} \quad (17)$$

Compared to equation 10, the Heaviside function was replaced with the Fermi function. At zero temperature, the equations agree. The zero temperature energy can subsequently be approximated by [38]

$$E(0) = \frac{1}{2}((E(T) + F(T)) \quad (18)$$

with the entropy

$$S(T) = -\frac{2k_B}{N} \sum_{k,n} (f_{k,n} \ln f_{k,n} + (1 - f_{k,n}) \ln(1 - f_{k,n})) \quad (19)$$

and the free energy

$$F(T) = E(T) - TS(T) \quad (20)$$

$F(T)$ and $E(T)$ are similar at low temperature, and the error should be relatively small when using $F(T)$ instead of $E(T)$. As was pointed out later [39, 40, 41], analytical gradients are, for the case of an occupancy according to the Fermi function, consistent with the free energy $F(T)$. This can be seen by computing the additional terms due to the entropy:

$$\begin{aligned} -T \frac{\partial S(T)}{\partial X} &= \frac{2k_B T}{N} \sum_{k,n} \frac{\partial f_{k,n}}{\partial X} \ln \frac{f_{k,n}}{1 - f_{k,n}} \\ &= -\frac{2}{N} \sum_{k,n} \frac{\partial f_{k,n}}{\partial X} (\epsilon_n(k) - E_F) = -\frac{2}{N} \sum_{k,n} \frac{\partial f_{k,n}}{\partial X} \epsilon_n(k) \end{aligned} \quad (21)$$

Here, it was exploited that $\frac{2}{N} \sum_{k,n} f_{k,n} = n_0$ in analogy to equation 14 and thus the derivative $\frac{2}{N} \sum_{k,n} \frac{\partial f_{k,n}}{\partial X} E_F = 0$. Another term is due to the derivative of the density matrix.

This leads now to an additional term:

$$\begin{aligned} &\sum_{j,\alpha,\beta} \frac{\partial E}{\partial P_{\beta\alpha}^{j0}} \sum_{k,n} \frac{\partial P_{\beta\alpha}^{j0}}{\partial f_{k,n}} \frac{\partial f_{k,n}}{\partial X} \\ &= \sum_{j,\alpha,\beta} \frac{\partial E}{\partial P_{\beta\alpha}^{j0}} \sum_{k,n} \frac{1}{N} \exp(ikja) \frac{\partial P_{\beta\alpha}(k)}{\partial f_{k,n}} \frac{\partial f_{k,n}}{\partial X} \\ &= \sum_{j,\alpha,\beta} \frac{2}{N} \sum_{k,n} \exp(ikja) F_{\alpha\beta}^{0j} c_{\alpha n}^*(k) c_{\beta n}(k) \frac{\partial f_{k,n}}{\partial X} \\ &= \frac{2}{N} \sum_{j,\alpha,\beta} c_{\alpha n}^*(k) S_{\alpha\beta}(k) c_{\beta n}(k) \epsilon_n(k) \frac{\partial f_{k,n}}{\partial X} = \frac{2}{N} \sum_{k,n} \epsilon_n(k) \frac{\partial f_{k,n}}{\partial X} \end{aligned} \quad (22)$$

But this term is just equivalent to the entropy term in equation 21, with opposite sign. As a whole, for the derivatives of the free energy with respect

to a geometrical parameter X , the two terms containing derivatives of the occupation number $\frac{\partial f_{k,n}}{\partial X}$ cancel, and the expression is:

$$\begin{aligned} \frac{\partial F}{\partial X} &= \frac{\partial E - TS}{\partial X} = \sum_{j,\mu,\nu} \frac{\partial H_{\mu\nu}^{0j}}{\partial X} P_{\nu\mu}^{j0} + \frac{1}{2} \sum_{j,\mu,\nu} \sum_{h,l,\tau,\lambda} P_{\lambda\tau}^{lh} P_{\nu\mu}^{j0} \frac{\partial ({}^{0j}_{\mu\nu} || {}^{hl}_{\tau\lambda})}{\partial X} \\ &- \sum_{j,\mu,\nu} \frac{\partial S_{\mu\nu}^{0j}}{\partial X} \sum_{k,n} \frac{2}{N} \exp(ikja) c_{\mu n}^*(k) c_{\nu n}(k) f_{k,n} \epsilon_n(k) + \frac{\partial E(NR)}{\partial X} \end{aligned} \quad (23)$$

This can be viewed as a generalization of the result in section 2.1, with the θ function being replaced with the Fermi function. At zero temperature, this reduces to the θ function, and the entropy becomes zero. These arguments hold similarly for the case of higher dimensions or the case of density functional theory.

For higher temperatures T , the forces and the derivative of the total energy deviate stronger, and a suggestion was made to remedy this, in order to obtain the derivative of the total energy, and not of the free energy [42].

3. Examples

In the following, some examples demonstrate the accuracy of the gradients. The calculations were done with the present CRYSTAL09 release [43, 1]. The examples aim at documenting the accuracy of the gradient, by comparing the analytical and numerical gradient, at the level of Hartree-Fock and density functional theory, for the gradient with respect to the cell parameter, and with respect to the nuclear position.

First, for Cu bulk, the analytical and numerical gradient with respect to the cell parameter are compared in table 1. This is done on the Hartree-Fock and density functional level. The basis sets from reference [44] were used. A \vec{k} -point mesh with $16 \times 16 \times 16$ points was used. Smearing temperatures in the range from $0.001 E_h$ to $0.05 E_h$ were chosen. Technically, in the input, a hybrid functional consisting of nothing but 100% Fock exchange was defined, in order to perform the Hartree-Fock calculation at finite temperature. When comparing numerical and analytical derivatives, then the obtained accuracy for the derivative of the free energy $-\frac{\partial F}{\partial a}$ is similar to the one for insulators, see [15, 16, 17, 18, 19]. Note that in addition, the numerical noise is in general larger in the case of metals, and therefore, also the energies and

Table 1: The derivative of the total energy and the free energy, in hartree/bohr (E_h/a_0), with respect to the cell parameter a , analytical and numerical, on the Hartree-Fock and density functional (LDA) level.

smearing temperature (E_h)	$-\frac{\partial E}{\partial a}$ (numerical) ($\frac{E_h}{a_0}$)	$-\frac{\partial F}{\partial a}$ (numerical) ($\frac{E_h}{a_0}$)	$-\frac{\partial F}{\partial a}$ (analytical) ($\frac{E_h}{a_0}$)
Hartree-Fock (at $a = 5 \text{ \AA}$)			
0.001	-0.0316	-0.0316	-0.0314
0.01	-0.0317	-0.0315	-0.0313
0.03	-0.0328	-0.0305	-0.0303
0.05	-0.0352	-0.0276	-0.0280
LDA (at $a = 3.4 \text{ \AA}$)			
0.001	0.0315	0.0315	0.0317
0.01	0.0310	0.0319	0.0320
0.03	0.0212	0.0390	0.0393
0.05	0.0098	0.0540	0.0542

their numerical derivatives carry larger noise. The agreement between analytical and numerical derivative of the free energy is similar for all smearing temperatures.

The derivative of the energy with respect to the cell parameter agrees reasonably well at low temperatures, but deviates strongly at high smearing temperatures, as expected, as the energy and the free energy deviate more and more at higher temperature. The free energy and its derivative with respect to the cell parameter are also visualized in figure 1, where a smearing temperature of $0.001 E_h$ was employed. Again, the agreement between numerical and analytical derivative is very good.

As an example for the gradient with respect to nuclear positions, the adsorbate system Cu(111)($\sqrt{3} \times \sqrt{3}$)R30°-Cl is considered, with chlorine sitting on the hcp (hexagonal close packed) site. The basis sets are as in [44], and $16 \times 16 \vec{k}$ -points together with a smearing temperature of $0.001 E_h$ is used. The free energy and its derivative with respect to the z-component of the

chlorine atom are computed analytically and numerically. The results are visualized in figure 2, and the numerical and analytical derivatives agree well. The computed equilibrium position corresponds to a height of 1.85 Å above the topmost Cu layer, in reasonable agreement with the earlier calculation [44]: in the earlier calculation, a generalized gradient functional had been employed and a height of 1.90 Å had been obtained. The present calculation gives a slightly shorter bond length which is a usual feature of the local density approximation (LDA), as compared to gradient corrected functionals. Note that no gradients had been used in the earlier work [44], and the geometry had been determined by iteratively optimizing the various geometrical parameters, by employing the total energy only.

4. Conclusion

Derivatives of the total and free energy of periodic systems with respect to geometrical parameters were studied theoretically, in the case of metallic systems. In the case of metals, numerical integration is often facilitated by introducing an artificial temperature and by an occupancy according to e.g. the Fermi function. At zero temperature, the theory of the derivatives does not require an additional term compared to the case of insulators. At finite temperature, when the occupancy is according to the Fermi function, then a similar expression for the derivative can be employed, which is however only consistent with the free energy. Therefore, numerical derivatives of the free energy agree reasonably well with analytical derivatives, and consequently, numerical derivatives of the total energy deviate more and more with increasing temperature. This holds for the case of Hartree-Fock or density functional theory. Numerical examples demonstrate the accuracy which is achieved with the implementation in the CRYSTAL code.

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Figure 1: Left: Free energy for Cu bulk; crosses refer to computed points, the full line is a fit through the points. Right: Analytical (crosses) and numerical derivative (full line) with respect to the cell parameter for Cu bulk. The numerical derivative is obtained as a derivative of the fit of the energy expression in the left figure. A smearing temperature of $0.001 E_h$ was applied.

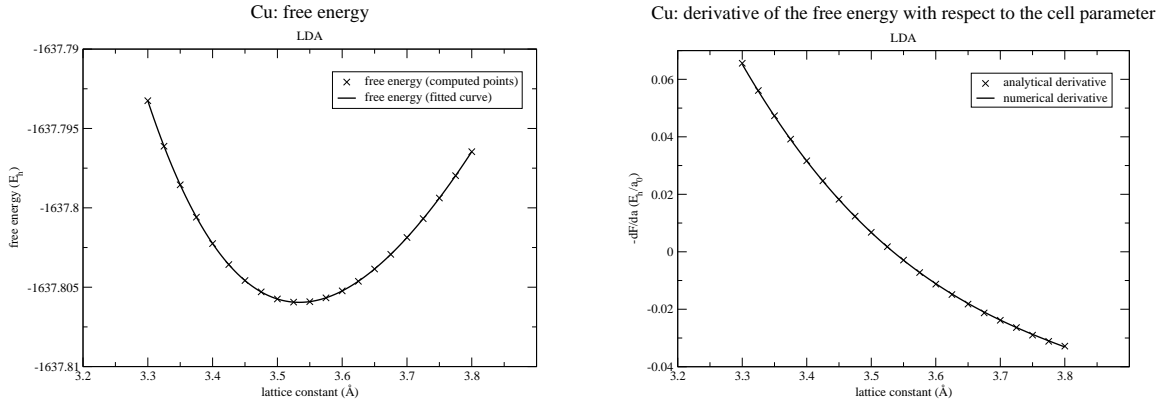


Figure 2: Left: Free energy for Cl/Cu(111); crosses refer to computed points, the full line is a fit through the points. Right: Analytical (crosses) and numerical derivative (full line) with respect to the z-position of the Cl atom. The numerical derivative is obtained as a derivative of the fit of the energy expression in the left figure. A smearing temperature of $0.001 E_h$ was applied.

